FIRST LAW

Energy can neither be created nor destroyed. It can only change forms.

- In any process in an isolated system, the total energy remains the same.
- A definate amount of mechanical work is needed to produce definite amount of heat and vive versa.

W/H= j. where j is called joules constant.

- The increase in the internal energy of a system is equal to the amount of heat added to the system, **plus** the amount of work done **on** the system.
- The increase in the internal energy of a system is equal to the amount of heat added to the system, **minus** the amount of work done **by** the system.

dU = Q – W

Q=heat add to system

W = work done by system

- The total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from state A to state B, it undergoes a change in the internal energy from EA to EB. Thus, we can write $\Delta E = E_B - E_A$

LIMITATIONS

Thermodynamics is a powerful approach toward understanding chemical reactions, but only provides part of the picture. Specifically:

- Thermodynamics only points the way
- Thermodynamics says nothing about how long it takes to get there

- The stoichiometric equation for the reaction says nothing about its mechanism

THERMODYNAMICS ONLY POINTS THE WAY: Chemical change is driven by the tendency of atoms and molecules to rearrange themselves in a way that results in the maximum possible dispersion of thermal energy into the world. The observable quantity that measures this spreading and sharing of energy is the free energy of the system. As a chemical change takes place, the quantities of reactants and products change in a way that leads to a more negative free energy. When the free energy reaches its minimum possible value, there is no more net change and the system is said to be in equilibrium.

The beauty of thermodynamics is that it enables us to unfailingly predict the net direction of a reaction and the composition of the equilibrium state even without conducting the experiment; the standard free energies of the reactants and products, which can be independently measured or obtained from tables, are all we need.

THERMODYNAMICS SAYS NOTHING ABOUT HOW LONG IT TAKES TO GET THERE: It is worth noting that the concept of "time" plays no role whatsoever in thermodynamics. But kinetics is all about time. The "speed" of a reaction — how long it takes to reach equilibrium — bears no relation at all to how spontaneous it is (as given by the sign and value of $\Delta G°$) or whether it is exothermic or endothermic (given by the sign of $\Delta H°$). Moreover, there is no way that reaction rates can be predicted in advance; each reaction must be studied individually.

THE STOICHIOMETRIC EQUATION FOR THE REACTION SAYS NOTHING ABOUT ITS MECHANISM: The term "mechanism" refers to, "who does what to whom". Think of a reaction mechanism as something that goes on in a "black box" that joins

reactants to products. The inner workings of the black box are ordinarily hidden from researchers, are highly unpredictable, and can only be inferred by indirect means.

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

- The first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not.
- First law does not specify that process is feasible or not.
- Practically it is not possible to convert the heat energy into an equivalent amount of work.

APPLICATION OF SECOND LAW OF THERMODYNAMICS

- All types of vehicles that we use, cars, motorcycles, trucks, ships, aeroplanes, and many other types work on the basis of second law of thermodynamics and Carnot Cycle. They may be using petrol engine or diesel engine, but the law remains the same.
- All the refrigerators, deep freezers, industrial refrigeration systems, all types of airconditioning systems, heat pumps, etc work on the basis of the second law of thermodynamics.
- All types of air and gas compressors, blowers, fans, run on various thermodynamic cycles.
- One of the important fields of thermodynamics is heat transfer, which relates to transfer of heat between two media. There are three modes of heat transfer: conduction, convection and radiation. The concept of heat transfer is used in wide range of devices like heat exchangers, evaporators, condensers, radiators, coolers, heaters, etc.

ADIABATIC PROCESS

- An adiabatic process transfers no heat
  - therefore $Q = 0$
- $\Delta U = Q - W$
- When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.
- When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

ISOTHERMAL PROCESS

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if ΔT is zero, $\Delta U = 0$
- Therefore, $Q = W$
  - Any energy entering the system (Q) must leave as work (W)

IRREVERSIBLE PROCESS

Irreversible processes cannot be undone by exactly reversing the change to the system.

Spontaneous processes are irreversible.

REVERSIBLE PROCESS

In a reversible process, the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

SPECIFIC HEAT AT CONSTANT PRESSURE (CP) :

The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Pressure is maintained CONSTANT.

SPECIFIC HEAT AT CONSTANT VOLUME (CV) :

The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Volume is maintained CONSTANT.

INTERNAL ENERGY

We have already discussed work and heat extensively, but a few comments are in order regarding internal energy. The internal energy encompasses many different things, including:

- The kinetic energy associated with the motions of the atoms,
- The potential energy stored in the chemical bonds of the molecules,
- The gravitational energy of the system.

It is nearly impossible to sum all of these contributions up to determine the absolute energy of the system. That is why we only worry about DE, the change in the energy of the system. This saves all of us a lot of work, for example:

- if the temperature doesn't change we can ignore the kinetic energy of the atoms,
- if no bonds are broken or destroyed we can ignore the chemical energy of the system,
- if the height of the system doesn't change then we can ignore gravitational potential energy of the system.

Our convention for DE is to subtract the initial energy of the system from the final energy of the system.

DE = E(final) – E(initial) = q + w

In a chemical reaction the energy of the reactants is E(initial) and the heat of the products is E(final).

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